RESILIENT PROSTHETIC MATERIALS*)

J. F. BATES and D. C. SMITH

The principal use of soft polymers in prosthodontics is for denture liners. A satisfactory material for this purpose has been sought for more than 60 years since the first use of natural soft rubber. About 20 years ago plasticised polyvinyl chloride (P.V.C.) was employed (1-4). Later softer acrylic polymers were used also (5, 6). More recently elastomers (synthetic rubbers) particularly the cold curing silicone type became available.

As a result of these developments these various polymers are available in numerous commercial forms. Many reports on individual materials have been made (7-14).

Since these plastics may serve a variety of purposes the requirements for an ideal material will depend on the particular application, e.g. retention in obturators will require a material which is highly elastic at room temperature, (high deformability and low permanent set) whilst the conditioning of traumatised tissue will demand a material which flows sufficiently at mouth temperature to conform accurately to the tissues (high permanent set). However, it is essential that all materials should be non-toxic and non-irritant; permanently soft; colour stable and non-staining; tasteless; abrasion-resistant; aesthetic, and dimensionally stable. They should possess also good bonding to the denture base, low water sorption, good shelf life and the technique should be simple.

In the present work, the production of durable liners for dentures was of major interest, and thus this report describes the laboratory evaluation of commonly-used materials from this point of view, and the results of a clinical trial of selected products in continuance of earlier work (11).

Experimental Materials

The materials investigated are listed in Table 1 according to their type together with the name of the manufacturer or supplier and their physical form. The materials were processed according to the manufacturers' instructions, but where polyvinyl chloride-acetate was used the following technique was employed: –

The polymer powder was mixed with plasticiser and epoxide stabiliser and heated at 100° C until a stiff paste was formed. The paste was mould-

*) After a paper read for the Nederlandse Vereniging van Tandartsen at april 19th 1963.

TABLE 1

RESILIENT DENTURE LINERS TESTED

Material	*Manufacturer*	*Form*
Heat Curing Acrylic Type		
Palasiv	Kulzer & Co., Germany.	Powder-liquid
Neo-plastupalat	Farbenfabriken Bayer A.G. Germany.	Preformed sheet and liquid
Cold Curing Acrylic Type		
Coesoft	Coe Laboratories Inc., U.S.A.	Powder-liquid
Cora-line	Coralite Dental Products, U.S.A.	,, ,,
Durabase	Reliance Dental Mfg. Co. U.S.A.	,, ,,
Flexene	Cosmos Dental Products Inc., U.S.A.	,, ,,
Soft Oryl	The William Getz Corporation, U.S.A.	,, ,,
Heat Curing Silicone Type		
Molloplast B	Köstner and Co., Germany.	Premixed Dough
Cold Curing Silicone Type		
Flexibase	Flexico Developments Ltd., U.K.	Paste and liquid activator
D.P. Silyne	Dental Perfection Co. Inc., U.S.A.	,,
Verone R.S.	Davis, Schottlander and Davis, U.K.	,,
Polyvinyl Chloride-Acetate Type		
Corvic S.U.	Dental Manufacturing Co., U.K.	Powder and plasticiser

ed in a frame mould in an electrically heated hydraulic press and gelled at 140° C for 5 minutes. Sheets of 1.5 mm. and 3 mm. thickness were prepared using dibutyl phthalate (DBP) and dioctylphthalate (DOP) in 50% and 70% concentration by weight. The sheet material was bonded to the acrylic dough using an adhesive paste of 40% methyl methacrylate, 10% polymethyl methacrylate and the balance P.V.C.A. Previous work by Bains (15) and Smith (16) had shown this to be the best method of obtaining optimum properties from the material.

EXPERIMENTAL METHODS

Laboratory Tests

Specimen Preparation

Two series of flat 5 cm. square specimens were made, having thicknesses of 1.5 and 3.0 mm. respectively of elastomer bonded to a 1.5 mm. thickness of a regular heat cured acrylic denture base material (Kallodent 333). For Neo-plastupalat a long doughing material (Virilon) was employed instead. These specimens and portions of them were used in all tests except compression set and strain and bond strength. The specimens were conditioned in air for 7 days or in water for 30 days after processing. At least three determinations were made in each test and the results averaged.

Water Absorption

The water absorption was estimated by storing specimens in water at 37° C for 30 days. The elastomer was then stripped off and the loss on drying to constant weight over phosphorus pentoxide determined. Measurements of weight increases on absorption are not informative since the values are influenced by leaching out of plasticisers from some materials and loss of gas from others, e.g. cold curing silicones.

Oil Absorption

The elastomer layer was removed from two sets of water saturated specimens as above. One set was immersed individually in olive oil, the other in oil of peppermint. The specimens were removed at intervals, blotted dry, and weighed. The weight increases were taken as the comparative oil absorption.

Light Stability

One half of a wet specimen was exposed to the radiation from a combined tungsten-mercury vapour lamp for 24 hours under the condition of British-Standard 2487 (acrylic denture base material). The exposed and unexposed areas were compared visually. Another series of specimens were assessed similarly after 30 days storage in water at 37° C in daylight.

Bond Strength

Tensile specimens of 6 mm. square cross section were prepared which contained a central segment of the elastomer in the gauge length (Fig. 1). The load required to rupture the specimens at room temperature was determined after 24 hours in water at 37° C, using a Hounsfield Tensometer and an extension rate of 2″ per minute. A "bond strength" was calculated on the original cross sectional area. (This test gives information on the strength of the joint in comparison to the strength of the material. A peel or tear test has less easily definable conditions). The nature of the interface between the elastomer and base resin was examined microscopically using smoothed sections of the flat specimens.

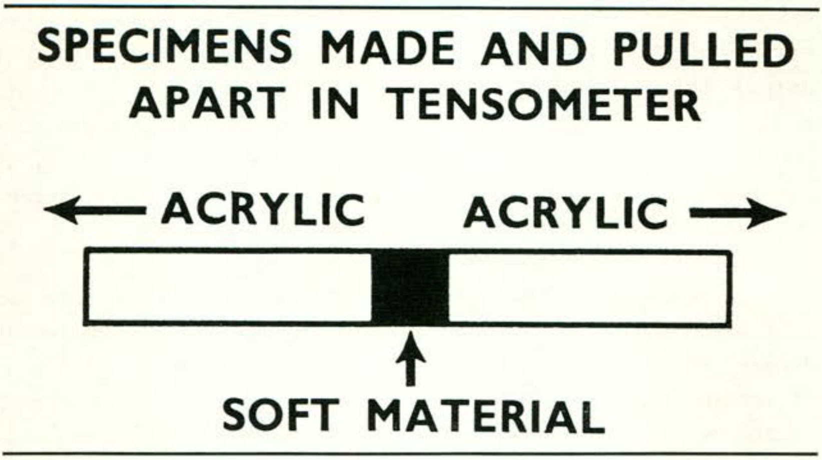

Fig. 1. Diagram of the bond strength specimens.

Hardness

Hardness was determined from the surface penetration of a 3/32″ ball under an initial load of 30 g. with vibration for 5 secs. followed by a 540 g. load for 30 secs. The method was similar to British Standard 903 (Vulcanised Rubber). Results were obtained on wet specimens.

Compression Set and Strain

The strain in compression (a measure of stiffness) and the compression set (a measure of elasticity) were determined on specimens of 0.75″ high and 0.5″ diameter prepared in a gypsum mould. Tests were carried out at 37° C in water using the procedure described in A.D.A. Specification No. 11 (Hydrocolloid impression material).

Effect of Denture Cleansers

The effects of representative types of denture cleanser on colour and surface was assessed visually and on hardness using the procedure previously described.

Clinical Tests

Preliminary trials of the materials on the European market were made. Subsequently two materials were used for more extensive trials. A total of 89 patients were examined at 9 monthly intervals over a period of three years. A further 30 patients have been treated with a third material but for 9 months only.

TABLE 2

WATER ABSORPTION OF RESILIENT MATERIALS

Material	*Loss of weight on drying* %
Palasiv	2.7
Neo-plastupalat	2.6
Coesoft	1.0
Cora-line	3.2
Durabase	3.6
Flexene	4.0
Soft Oryl	2.6
Molloplast B	3.8
Silyne	0,6
Verone R.S.	3.3
Corvic SU/DOP 50%	2.5
Corvic SU/DOP 70%	4.1

RESULTS AND DISCUSSION

Water Absorption

Table 2 shows the results for weight loss on drying the 1.5 mm. thick specimens. Similar results to those of Table 2 were obtained for the 3 mm. specimen. The value for the Corvic S.U. was higher than was anticipated but very similar results were obtained by HERRMAN (8). Some of the silicone materials showed unexpectedly high results for this type of material, but this was perhaps due to the type of filler used.

A large water absorption may lead to swelling and stresses at the denture base interface which would tend to promote reduction in bonding and distortion. The rate of diffusion of water through the material is also of importance in the latter respect. No data could be obtained for this factor but it was noteworthy that the cold curing silicone plates showed the most warpage. Ideally both the rate of diffusion and total water absorption should be close to that of the acrylic base material which in the present case was 2.2%. Table 2 shows that the heat cured acrylic types were closest to this figure.

Oil Absorption

The data in Table 3 shows quite different behaviour for the two types of oil. Olive oil tended to extract plasticiser and little swelling was observed. Peppermint oil was rapidly absorbed with considerable swelling.

TABLE 3

OIL ABSORPTION OF RESILIENT MATERIALS

Weight Absorption at Saturation

Material	*Olive Oil* %	*Peppermint Oil* %
Palasiv	—0.5	+275
Neo-plastupalat	+0.6	+380
Coesoft	—12.2	+86
Cora-line	—5.6	+72
Durabase	—4.2	+41
Flexene	—3.5	+166
Soft Oryl	—9.6	+38
Molloplast B	—3.1	+45
Flexibase	—3.8	+23
Silyne	—0.6	+32
Verone R.S.	—3.2	+24
Corvic SU/DOP 50%	—13.5	+8.9[a]
70%	—38.0	—11.8[a]

[a] After 21 days the specimens were not at equilibrium.

The silicone compositions showed the best allround resistance, the cold curing acrylic materials were less satisfactory. This test is important in relation to resistance to fatty foods, denture cleaners, mouthwashes and other sources of essential oils. The heat cured acrylic materials and the silicones reached a constant loss with respect to olive oil after seven and twelve days respectively. The former fell to the stated value after a larger gain in the first twenty-four hours. The cold curing acrylic materials continued to lose weight though more slowly after twelve days. The silicone materials lost weight slowly in peppermint oil after the initial absorption. All other materials continued to absorb until the approximately constant values of Table 3 were reached.

Light Stability

Most materials were stable under the two sets of test conditions. Slight yellowing with some of the cold curing acrylic materials was probably due to polymerisation promoters. A whitish surface was produced on the cold curing silicones possibly due to chemical reaction of water with the surface. A milky appearance of the Corvic S.U. was due to water absorption and was reversible.

TABLE 4

BOND STRENGTH OF RESILIENT MATERIALS TO ACRYLIC BASE MATERIAL

Material	*Bond Strength* p.s.i.	*Fracture Site*
Palasiv	300 ± 40	M
Neo-plastupalat	" 800 ± 40	B
Coesoft	+ 110 ± 30	M
	++ 150 ± 20	M
Cora-line	120 ± 5	M
Durabase	—	—
Flexene	260 ± 60	M and B
Soft Oryl	110 ± 20	M
Molloplast B	180 ± 30	M
Flexibase	150 ± 20	B
Silyne	80 ± 10	B
Verone R.S.	30 ± 10	B
Corvic DOP/70%	860 ± 40	M

" Special acrylic material
\+ Cold cured
++ Heat Cured

M = Fracture in material
B = Fracture in bond

Bond strength

The data of Table 4 shows that the most tenacious bond was obtained with the P.V.C.A. material. In this case and others the bond was stronger than the material. Neo-plastupalat gave results 50% lower when used with the standard acrylic base material. These wet specimens showed only a small decrease in strength compared to dry specimens except for the cold curing silicones which showed a drop of about 30%.

All the materials gave what was apparently a clinically satisfactory bond strength except the cold curing silicones. The bond with these materials was greatly dependent on experience. Correct application of the primer and application of pressure to the paste when some thickening had occurred were very important. An assessment of the technique for each material is provided by the deviation in bond strength. In early series of tests on these silicones, deviation of ± 70 p.s.i. were recorded. Use of D.B.P. with Corvic S.U. did not give improved results compared to D.O.P. A Corvic/D.O.P. paste cured at 100° C with the acrylic dough

TABLE 5

HARDNESS (B.S.H.°[a]) OF RESILIENT MATERIALS

Material	1.5 mm. Thickness 20° C	1.5 mm. Thickness 37° C
Palasiv	55	39
Neo-plastupalat	65	45
Coesoft	36	33
Cora-line	55	36
Durabase	46	37
Flexene	44	38
Soft Oryl	53	53
Molloplast B	61	59
Flexibase	64	61
D.P. Silyne	61	54
Verone R.S.	65	61
Corvic/DOP 50%	74	66
Corvic/DOP 70%	65	61
Acrylic base material	100	100

[a] British Standard Hardness

gave results one third of those quoted, whereas dry heat at 140° C in a dry gypsum gave two thirds the strength in Table 4.

Complete bonding over the whole of larger areas could not be consistently achieved with the cold-curing silicones. This was borne out by microscopic examination of the sectioned specimens which showed this variability of bonding. Materials cured against the acrylic dough, e.g. Neo-plastupalat, Palasiv, Molloplast B, Corvic S.U., showed a very intimate contact with a diffuse boundary; compatible materials bonded to the precured base, such as Soft Oryl and Flexene showed a sharper demarcation whereas the cold curing silicone materials showed a distinct demarcation, or actual separation where bonding was deficient.

Hardness

The hardness figures for wet specimens in Table 5 are a measure of resistance to slow penetration and are not proportional to the hardness of the base material. A lower figure means a less hard (i.e. softer) material. The acrylic type materials were much softer at mouth temperature whereas the silicone materials were little affected. For very soft materials such as Coesoft, or Soft Oryl, the precise value was difficult to determine since the material was completely penetrated to the hard base. Variable hard-

TABLE 6

EFFECT OF THICKNESS ON HARDNESS OF RESILIENT MATERIALS AT 20° C

Material	*Hardness B.S.H.°*	
	1.5 mm. Thickness	*3 mm. Thickness*
Palasiv	58	45
Neo-plastupalat	65	42
Flexene	47	34
Soft Oryl	53	14
Molloplast B	53	42
Flexibase	65	55
Verone R.S.	60	58
Acrylic Base Material	100	100

ness was encountered in specimens of Neo-plastupalat due possibly to variations in the monomer absorption during processing, and in the cold curing silicones probably because of non-uniformity in mixing the base paste and activator. The apparent hardness of specimens was also increased by decreasing thickness (Table 6), the greatest response being shown by the acrylic materials. From a practical point of view this was

TABLE 7

COMPRESSION STRAIN AND SET OF RESILIENT MATERIALS AT 37° C

Material	*Compression*	
	Strain %	*Set* %
Palasiv	12.9	1.1
Neo-plastupalat	20.7	3.8
Coesoft	26.8	6.5
Cora-line	11.9	2.8
Durabase	13.5	2.5
Flexene	15.5	2.1
Soft Oryl	29.4	13.4
Molloplast B	6.6	0.4
Flexibase	4.4	0.07
Silyne	7.2	0.02
Verone R.S.	7.9	0.3
Corvic SU/DOP 50%	5.0	0.4
Corvic SU/DOP 70%	19.7	0.9

TABLE 8

EFFECT OF DENTURE CLEANSERS ON RESILIENT MATERIAL

Material	*Cleanser Type*			
	Water	*Oxygenated*	*Acid*	*Hypochlorite*
Palasiv	—	—	—	Bleached
Neo-plastupalat	—	—	—	,,
Coesoft	sl. orange	sl. orange	sl. orange	,,
Cora-line	—	—	,,	,,
Durabase	—	sl. orange	,,	,,
Flexene	—	—	,,	,,
Soft Oryl	sl. orange	surface bubbles	,,	,,
Molloplast B	—	—	—	Heavily bleached
Flexibase	Whitish surface	Whitish surface	—	Bleached surface
Silyne	—	—	—	Bleached
Verone R.S.	—	—	—	Bleached
Corvic/DOP 70%	milky	—	—	—

— = no change
sl. = slight

important as a source of clinical variability which was not easily controllable between dentures using a particular material. The optimum hardness for a liner is not known however.

Compression Strain and Set

The compression strain, (Table 7), is a measure of stiffness and the set is a measure of elasticity. In both respects there was a sharp division between the silicones and the other materials. The acrylic materials exhibited a degree of flow and the deformation was time dependent whereas the silicones gave an approximately constant strain and recovered almost completely within a few seconds.

The greater stiffness of the silicone materials was also reflected in the penetration hardness, (Table 5). The two classes of material provided a choice of an elastic behaviour or a more leathery quality. Control of the plasticiser content with the P.V.C.A. allowed the use of a soft material with good elasticity.

Effect of Denture Cleansers

Table 8 shows the effect of common types of denture cleanser used according to the manufactures' directions for six weeks. The specimens

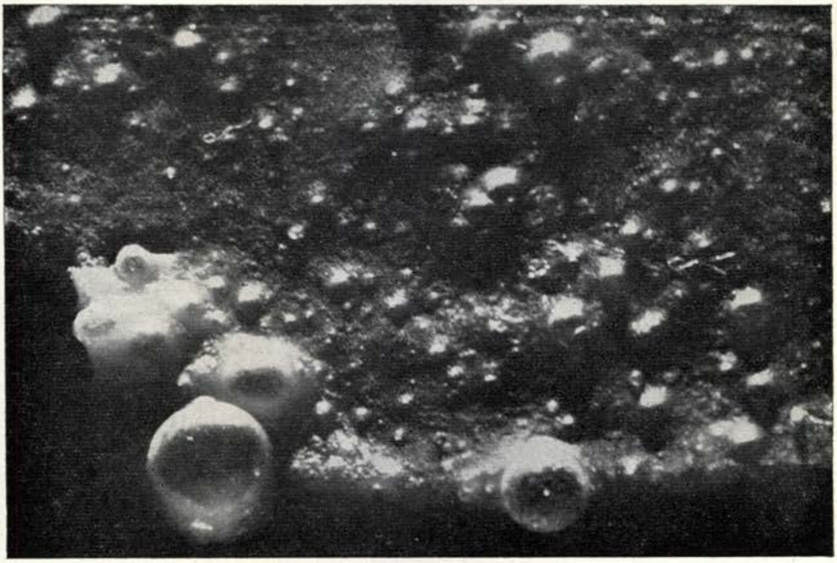

Fig. 2. Surface of a sheet of „Palasiv" soaked in denture cleaner for 6 weeks, according to the manufacturer's instructions. (× 4).

were cut from a sheet of each liner made without an acrylic backing. Cleansers of the dilute mineral acid type had no surface effect on any of the materials. The oxygenated type caused bubbling of the surface, with the cold-curing acrylic materials and also with the heat-curing materials if used warm (60° C) as some manufacturers instructed (Fig. 2). Softening was also observed, probably due to absorption of peppermint or other oils as evidenced by odour pickup.

TABLE 9

EFFECT OF DENTURE CLEANSERS ON HARDNESS OF RESILIENT MATERIALS AT 20° C

Material	*Oxygenated Type*			*Water*	*Acid Type*
	Steradent	*Oxydent*	*Milton*		*Dentry Bleach*
Palasiv	51	44	50	45	51
Flexene	35	36	39	34	35
Soft Oryl	42	44	—	47	48
Molloplast B	44	48	39	42	52
Flexibase	51	53	55	55	49
Verone	45	54	44	58	58

This was confirmed by the effects on the hardness (of a 3 mm. thick layer of the materials) of treatment for 6 weeks with various cleansers (Table 9). The alkaline oxygenated type in general increased the hardness probably due to plasticiser extraction predominating over oil absorption although each cleanser had an individual effect. The acid cleanser caused some hardening also except for one of the cold-curing silicones. The data suggests that none of these types of commercial cleansers is suitable for these resilient materials.

CLINICAL TRIALS

Preliminary

Parallel with the laboratory testing of the materials, clinical trials were carried out and it soon became obvious that some materials, whilst performing adequately in the laboratory tests, were not satisfactory when used in the mouth.

In order to obtain a stable product with plasticised P.V.C.A. it is necessary to gel the material and plasticiser at 140° C under dry conditions. Production of a denture under such conditions is not desirable and thus preformed sheets of the material were made and cemented into the denture. Failures occurred because the deformation of the sheet over the ridge resulted in residual stress and breaking of the bond. If the dough of P.V.C.A. was packed and cured with the denture a partially gelled product resulted which in two or three months lost its plasticiser, probably by migration into the denture base and extraction by saliva, with hardening and cracking of the material.

The *cold curing silicone* materials all failed to bond consistently over the whole of the curved irregular surface of the dentures, in spite of an adequate bond strength under the simpler conditions of laboratory testing.

The *heat cured acrylates* were very satisfactory although in the case of Neo-plastupalat the material necessitated a very time-consuming technique.

The *cold cure acrylates* became orange readily and in the case of Soft Oryl, rough and blistered soon after insertion. Flexene as originally supplied was too hard and did not sufficiently relieve the clinical condition. In a later form it occasionally split along the ridge suggesting loss of plasticiser.

As a result of these trials and the laboratory tests, the two materials which appeared the most suitable were Molloplast B and Palasiv. Since they had very different physical properties, it was decided to carry out more extensive trials with both these materials. During these trials heat cured Flexence became available and a further series of cases was begun using both this and the cold-curing type of this material. Direct relining was considered inadvisable as a) moisture may reduce the bonding, b) the material may be irritant or toxic, c) the thin areas of soft tissue where the greatest thickness of lining is required obtain quite the reverse. It is these "hard areas" which first touch the denture when it is seated that need the greatest thickness of liner.

Main Trial

Technique

All the liners were processed onto the dentures in the laboratory with a similar technique for both materials. It was found to be very important to allow the acrylic dough to stiffen for several hours before packing the soft lining in order to avoid porosity in the latter.

Molloplast B, like other silicone elastomers, was difficult to polish but could be smoothed with special stones*) to a satisfactory finish.

Clinical Examination

The linings were inserted in dentures from 1960 onwards and each patient was examined at approximately 9 monthly intervals from the date of insertion of the dentures. A total of 89 patients was kept under observation. 36 of these had Molloplast B linings and the remainder Palasiv.

The procedure of examination was constant throughout as follows:

1) Examination of oral tissues.
2) Assessment of oral hygiene.
3) A record of the patients' comments was made with special reference to comfort, taste and any comparisons with previous linings.
4) The method of cleaning was established.
5) The lining was examined for colour, abrasion, deposit and bonding.
6) The hardness in 1/1 and 4/4 regions was measured.

Results

(1) *Patient Comfort*

Sixty per cent of the patients in both groups expressed an opinion that they were more comfortable and had less pain. With Palasiv, ten per cent said they were worse whilst only one patient with Molloplast B expressed the same opinion. The silicone material was not „wetted" by the saliva to

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*) Dedeco, U.S.A.

het same extent as the acrylate materials and when extended as a periphery leads to an unpleasant feeling as the moving tissues slide over the surface. Where possible, "boxing-in" of the material was therefore desirable.

(2) *Mucosal Irritation*

These patients were treated because of the tenderness of the oral soft tissues and the rapidity with which soreness and ulceration developed when wearing conventional acrylic dentures. Difficulty was found in distinguishing between soreness resulting from the resilient material itself or the failure of the material to relieve normal soreness exhibited with hard dentures. From a clinical examination it was thought that all the cases were of the latter type. No evidence of allergy or local chemical irritation was observed. Approximately 20% of patients showed some tissue irritation which, as expected, could not be correlated with the comments made regarding comfort.

(3) *Taste*

This was a transient feature and disappeared in under two weeks. It appears slightly more pronounced in Palasiv (40%) than with Molloplast B (30%).

(4) *Effects of Wear on the Lining*

Fig. 3 shows the results obtained with the two materials. Usually the Molloplast B survived better in that the surface remained cleaner and smoother. Loss of colour was often due to a "waxy bloom" which could be removed in an acid cleaner. There appeared to be no bubbling of the surface due to a combination of heat and oxygen cleaners as with Palasiv (Fig. 2).

The most unsatisfactory feature of the Palasiv material was the roughening of the surface in a large number of cases and the ease with which food particles could be embedded in the surface. It was felt that the principal cause of deterioration was due to the absorption of essential oils from the cleaners used and the loss of plasticiser, although in some cases deterioration occurred when no cleaning materials had been used. Palasiv '62' has been recently introduced and is said to overcome the faults observed in this survey.

Attempts to correlate the hardness of the lining with the cleaning method failed, as the range of hardness values was too great due to the variation in thickness. There were numerous variables involved which

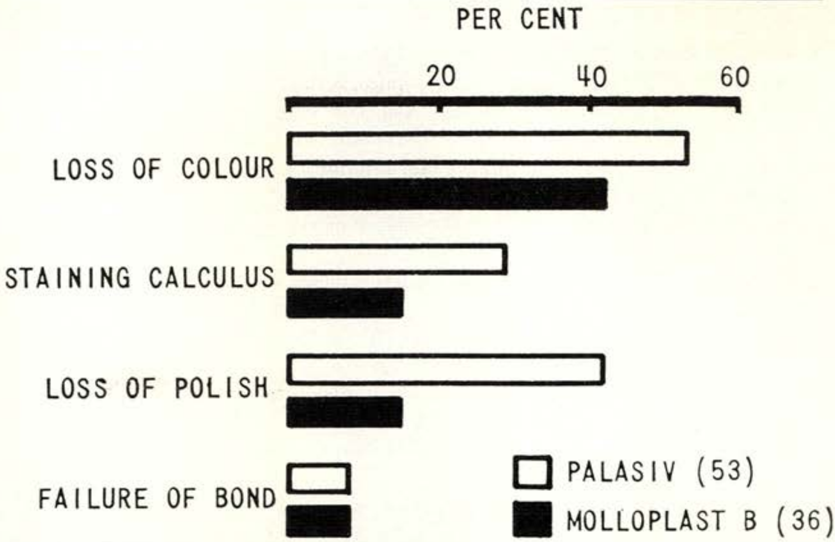

Fig. 3. Histogram comparing the effects of clinical wear on Molloplast B and Palasiv denture linings.

might have influenced the hardness, e.g. extraction of plasticiser and absorption of oil of peppermint which, as shown previously, would cause swelling of the lining.

After 6 months to one year's wear, 30 Flexene liners appear to be showing similar features to Palasiv.

Conclusions from the Survey

The conclusions from this survey were as follows:

(1) The material Molloplast B, if treated correctly in the laboratory and by the patient, will survive a period of three years or more. It is essential to clean it with a mild abrasive, (e.g. $NaHCO_3$) and occasionally in an acid type cleaner.

(2) No decision could be made regarding the ideal type of material for this type of treatment, i.e. a purely elastic material or a more plastic type of material. It was expected that the patients' comments on comfort would enable a decision to be made but both materials appeared to be clinically satisfactory.

(3) The authors feel that sufficient evidence is available to prove the need for a resilient plastic material and that progress in this field should lead to a material with a life expectancy comparable to the denture base.

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